Coal Hydrogenation Char as Blending Agents for Coke Production

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Metallurgical coke, necessary in the production of "hot metal" in the conventional blast furnace, requires large quantities of coal with specific physical properties. These coals are expensive because of their relative scarcity in comparison with non- or marginally coking coal. For many years blast furnace practice, the world over, has utilized minimum amounts of premium coals by blending coals with different properties to produce a mix that will give an acceptably strong and porous coke.(1) In some areas of the world, Japan for example, as many as 15 different coals may be blended to provide an acceptable mix.(2) These coals are purchased in Canada, Australia and the United States and only small quantities of Japanese coals are used because of their marginal coking quality. Practice in the United States requires the use of minimum quantities of premium coals and maximum use of marginally coking coals.

As an example of the U.S. situation, U.S. Steel's Geneva Works, near Provo, Utah, uses a blend of three coals to produce coke with a stability factor (percentage of the original coke remaining at a preselected screen size, following a fixed tumbling sequence) that is known to be required for iron production with a fixed blast furnace ore, limestone and coke feed. Captive coal from U.S. Steel's Geneva, Utah, and Somerset, Colo., mines (nearly equivalent in coking properties) are blended with 20% to 30% of coal from the Mid-Continent Coal & Coke Co. mine at Coal Basin, Colo. The Geneva and Somerset coals are high volatile bituminous in rank, with very low fluidity (1-5 dial divisions per minute in a Grisler Plastometer) and only minimum coking character as evidenced by a Free-Swelling Index of no more than 1. The Coal Basin coal is a medium volatile bituminous material with plasticity of more than 20,000 dial divisions per minute and a Free-Swelling Index of 3 or 4.

The present study is a laboratory scale examination of the possibility of using coal liquefaction char residues as a blending material with marginally coking coals to enhance the desired properties of the resulting coke.

Experimental

Standard blends of U.S. Steel, Geneva, Utah, coal and Mid-Continent Coal & Coke Co., Coal Basin coal were used as the base case for comparison with cokes produced using Geneva coal with added amounts of residual chars produced in the University of Utah's entrained-flow coal liquefaction reactor.(3) Proximate and ultimate analyses of the reference coals and the tested chars are shown in Table 1 and 2. The hydrogenation reactor conditions, as well as pertinent information with respect to the production of chars are included in Table 3. Properties of resultant cokes tested were Free-Swelling Index, strength, CO_2 burnoff rate and combustion temperature. Because only small quantities of char are available it was not possible to make strength or stability tests at the scale ordinarily required. Free-Swelling Index measurements were made on coke buttons resulting from ASTM test D720 applied to coals and blends.(4) Strength comparisons were made by measuring the pressure in pounds required to break the coke buttons produced in ASTM test D720, a dead weight gage was used for this measurement. Since this test was performed at such a small scale the results can be considered to be qualitative in nature and large-scale tests would be required for actual extrapolation to blast furnace operation.

Carbon dioxide burnoff rates were measured by heating coke samples (1 gram) at

900° C in a flowing stream of CO_2 for 1 hour(5). Traces of oxygen were removed from the gas by passing it over a bed of hot copper turnings. The combustion temperatures were measured by heating a 1-gram coke sample in a stream of oxygen and noting the temperature at which a sudden increase in temperature was observed(6).

For each of the measurements made, a series of 3 to 6 replicates were made in an effort to improve the confidence in the final answer.

Results and Discussion

The original impetus for this study followed observation that some coal liquefaction chars show extreme swelling in the standard volatile matter test (ASTM Test D-3175-77). Some of these chars swell sufficiently to fill the entire crucible and thus indicate high fluidity in the plastic temperature zone. Figure 1 shows the Free-Swelling Index (FSI) of a variety of residual coal hydrogenation liquefaction chars as a function of the conversion level. These measurements were made with a single starting coal, Clear Creek, Utah, from Island Creek Coal Co.'s Utah #2 mine. The indication is that higher conversion leads to higher FSI numbers. Obviously, this function must peak out and descend with very high conversion when the remaining organic matter is insufficient to provide fluidity. However, in the 60- to 80%-conversion range the FSI numbers approach those of acceptable blending coals.

Figure 2 shows the effect on FSI of blending Coal Basin coal and two different chars with Geneva Coal. R-71 and R-85 chars were produced from the same starting coal. R-71 represents a conversion of 75% of the coal matter to liquids and gases while R-85 represents a conversion of 25%. The lower conversion char does not affect the FSI while the high conversion char produces the same change in FSI and as does the addition of the accepted blending coal. If FSI were the only criterion required for blending material then R-71 would make a good substitute for Coal Basin coal in the Geneva coke starting material.

In Figure 3 are shown the pressures required to break the coke buttons prepared in the FSI tests. In this case the low conversion char (R-85) produces coke buttons that are harder than those produced by the reference coal. The high conversion char (R-71) produces coke buttons that are weaker. It is tempting to say that a high conversion char should be added for increasing the plasticity of the blend and that a low conversion char should be added for strength. However, these tests are yet to be performed.

Table 4 contains the CO_2 burnoff rates of cokes produced at 70, 80 and 90% Geneva coal concentration for the reference coal and the two chars. The low conversion char approximates the standard blend in burnoff rate at 70% but is higher at 80 and 90%. The high conversion char is higher in burnoff rate at all concentrations.

Table 5 contains a similar comparison for combustion temperatures. At 70% concentration of Geneva coal the standard additive is considerably better (has a higher combustion temperature). At 80 and 90% the low conversion char has no advantage but the high conversion char is at least equal to the standard additive.

Addition of a high conversion char such as R-71 would result in addition of ash materials to the product coke. This is not desirable because of the additional slag produced in the blast furnace as well as the additional heat required from the coke to melt the slag produced by the ash. Considering the material of this study, a 20%-addition of Coal Basin coal would increase the ash from 5.0 to 5.3%. A 20%-addition of R-71 (22.1% ash) would increase this from 5.0 to 8.4%.

A formidable problem with the addition of these particular chars to coals for production of metallurgical coke is that $ZnCl_2$ was used as a catalyst in the hydrogenation-liquefaction procedure. Zinc is a very troublesome element if present in blast furnace feed materials. Its compounds are reduced in the hot portion of the blast furnace, the metal is volatilized to the cooler portions of the upper area of the furnace. It tends to condense as ZnO and blocks small passageways such that the flow of gases may be seriously restricted. The oxide also tends to react chemically with Al_2O_3 in the firebrick lining of the furnace. This causes expansion and spalling of the brick surface. Chlorine is likewise an undesirable component of blast furnace materials because of its corrosive effects[7].

The data of Table 6 show the effect of successive leaching steps on the zinc content of the high conversion char (R-71). Seven leaches with HCl will reduce the $ZnCl_2$ equivalent concentration to 0.3% or 0.15% Zn. As a 20% component of the coal blend this would constitute only 0.03% Zn and would be quite acceptable.

It is apparent that some coal liquefaction chars do possess physical and chemical characteristics that would be desirable in coal blends used for the production of metallurgical grade coke. These are fluidity, strength and combustion temperature. The CO_2 burnoff rate was not improved by the addition of the chars used in this study.

ACKNOWLEDGEMENT

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Table 1. - Proximate analysis of coals and chars

	% H_2O	% Ash	% Volatile matter	% Fixed carbon
Coal Basin, Colo.	1.1	6.5	24.0	68.4
Geneva, Utah	3.2	5.0	39.6	52.2
R-71	2.4	22.1	24.8	50.7
R-85	2.7	8.4	39.6	49.3

TABLE 2. - Ultimate analysis of coals and chars

	% C	% H	% N	% S	% O	% Zn
Coal Basin, Colorado	84.3	5.0	2.1	0.7	1.4	--
Geneva, Utah	72.0	5.0	1.7	.7	15.6	--
R-71 Clear Creek, Utah coal char	49.2	3.7	1.8	.4	6.8	16.0
R-85 Clear Creek, Utah coal char	72.8	5.4	1.8	.7	4.9	6.0

TABLE 3. - Hydrogenation conditions and product description for Clear Creek, Utah coal chars used in this study.

	R-71	R-85
Coal sample weight, grams	852.3	626.6
Weight $ZnCl_2$ grams	57.1	41.6
Weight ash, grams	90.6	59.8
Total sample, grams	1,000	728
Particle size, mesh	-100+200	-200
Temperature, ° C	493	493
Pressure, H_2	1,800 psi	1,800 psi
Reactor length, ft	66	86
Average residence time	50 sec	10 sec
% Solids (after toluene extraction)	24.3	74.1
% Liquids produced	71.9	19.4
% gases	3.8	6.5
% Conversion	75.7	25.9

TABLE 4. - CO_2 burnoff rate of coal-char blends

% Geneva coal	70 mg/g/min	80 mg/g/min	90 mg/g/min
Coal Basin Coal	3.25	4.33	5.00
R-85	2.97	5.75	6.31
R-71	4.70	4.80	8.67

TABLE 5. - Combustion temperatures of coal char blends, ° C

% Geneva Coal	70	80	90
Coal Basin Coal	687	660	611
R-85	649	603	594
R-71	647	670	654

TABLE 6. - Effect of Zn removal from char on FSI

Char R-71 16.0% $ZnCl_2$ content

No. of Conc. HCl leaches*	%$ZnCl_2$	FSI
1	11.5	5.5
2	8.6	5.5
3	5.6	5.5
4	3.5	5
5	1.9	5
6	0.5	4
7	0.3	4

* Each leach 1 hour at boiling temperature (12 m HCl)

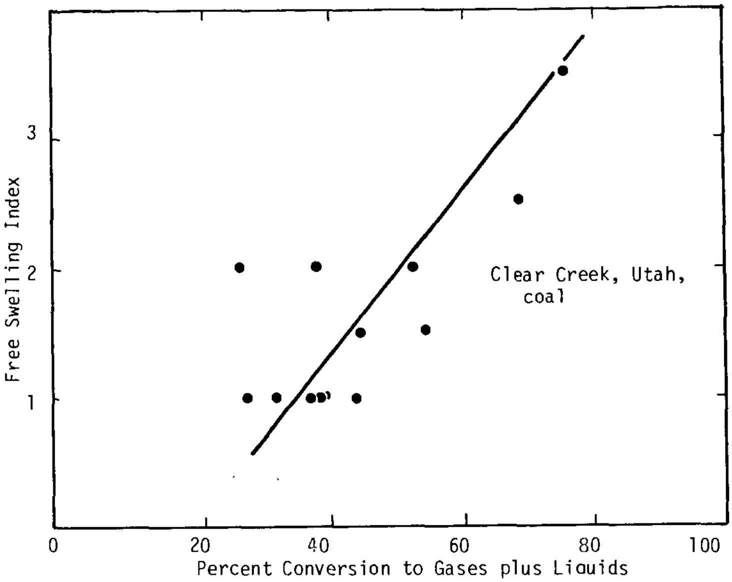

Figure 1. Capicity Hydrogenation Chars vs. Conversion Level.

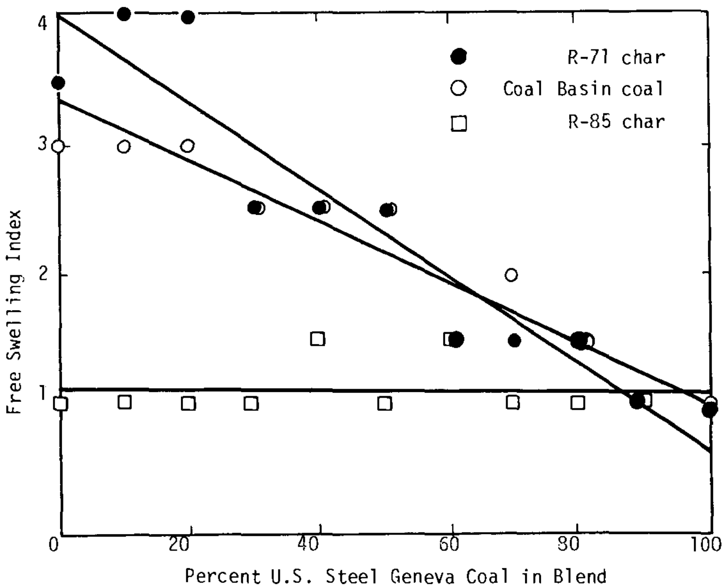

Figure 2. Swelling Capacity of Coal Blends.

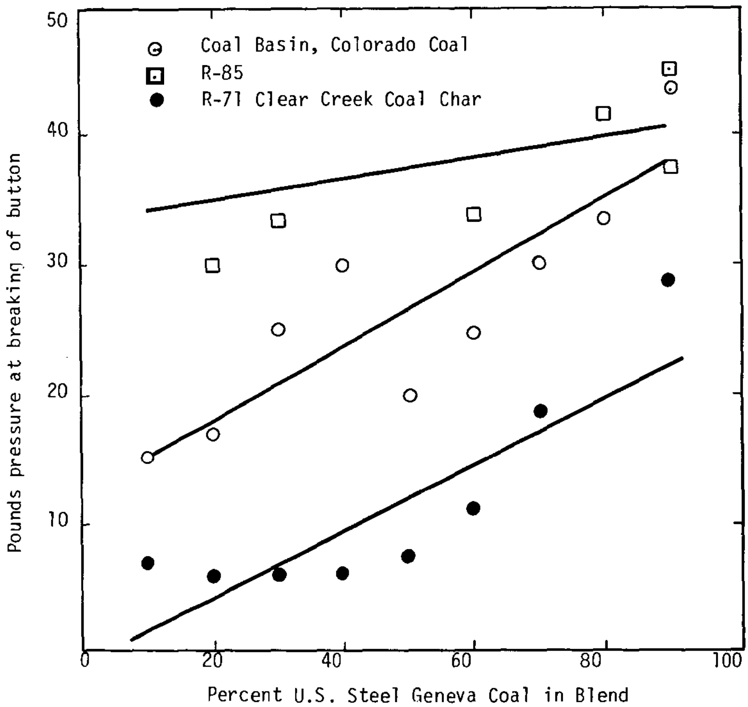

Figure 3. Breaking Pressure in Pounds for Volatile Matter Test Button.